

Effect of Sintering Aid on CGO Electrolyte for the Fabrication of Low Cost, Structural-controlled Solid Oxide Fuel Cell

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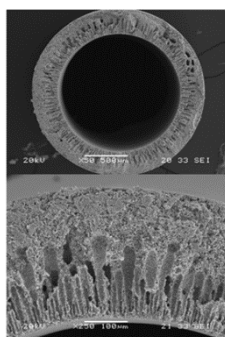
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Graphical abstract



Abstract

This paper reports the effort in reducing sintering temperature of cerium gadolinium oxide (CGO), a common intermediate temperature solid oxide fuel cell (SOFC) electrolyte, by doping it with lithium nitrate (LiNO_3) at 1, 2 and 3 mol%. LiNO_3 -CGO/NiO-CGO electrolyte/anode dual-layer hollow fibre (HF) for micro-tubular SOFC has been developed in this study via brush painting technique. The developed dual-layer HFs, which are co-sintered at 900-1250°C with the interval of 50°C, characterized by mechanical strength and microstructural analysis. Benefit of this study is the reduction of the sintering temperature, which eventually contributes to the fabrication of low-cost SOFC. Moreover, brush painting technique provides great adhesion between anode and electrolyte layer during sintering. With the increasing sintering temperature and content of LiNO_3 , densification and the mechanical strength of the developed dual-layer HF increased. Based on the experimental works, a sintering temperature of 1150°C with 3 mol% of LiNO_3 as sintering additive is recommended for the construction of the low cost dual-layer micro-tubular SOFCs.

Keywords: Cerium-gadolinium oxide (CGO); lithium nitrate (LiNO_3); sintering aid, micro-tubular solid oxide fuel cell (MT-SOFC); sintering temperature

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1.0 INTRODUCTION

Fuel cell has drawn attention of many people in past few years. This technology has been regarded as an alternative to resolve the depletion of the natural resource, global warming and green house effects. Fuel cell is a device which converts chemical energy from fuel to electrical energy through chemical reaction [1]. Fuel cell generally consists of three main components namely cathode, anode and electrolyte. Cathode is the positive side meanwhile anode is negative side. Electrolyte is the medium that allows the movement of the charges between both sides. Electrolyte can also be considered as a catalyst since it speeds up the reaction between the two electrodes. In general, the fuel discharges electron at anode and becomes positive. Electrolyte is designed in such way in order to allow only ions to pass through but not the electrons. The electron travels through the wires which eventually creates electric current flow [2]. Ions travel through the electrolyte and reach the cathode where it reacts with electron and another chemical, normally oxygen to produce water. However, solid oxide fuel cell (SOFC) operates in the different manner where reduction of oxygen occurs at cathode. These ions

later diffuse through the electrolyte and electrochemically oxidise the fuel at anode [3]. Among all types of fuel cell, SOFC has attracted great interest as it possesses so many significant advantages compared to other types of fuel cell. Some of the advantages of SOFC are greater tolerance to thermal cycling, quicker start up capability, higher volumetric output density and many more: [4-5].

Initially, SOFC operated using Yttria Stabilized Zirconia (YSZ) as the primary material for electrode and electrolyte. YSZ possesses high oxygen-ion mobility and negligible electronic conduction within the temperature range of 700-1000°C due to its high oxygen vacancy concentration [1]. Apart from having excellent thermal and mechanical stability, YSZ also chemically stable in both oxidizing and reducing conditions. However, in current situation, it is widely accepted that, long-term stability is very vital to achieve commercialization in SOFCs. Long term stability can be obtained primarily by minimizing material degradation by using alternative electrode and electrolyte materials which perform comparably high power densities and importantly operating at intermediate temperature which is 500-700°C [4].

Of the many materials with the potential to be used as a SOFC electrolyte at intermediate temperature, cerium-gadolinium oxide (CGO) has one of the highest ionic and higher thermal expansion coefficient which is more compatible with anode metallic components and cathode materials [6]. However, it is still difficult for CGO to be densely sintered below 1500°C by the conventional method. High sintering temperature of electrolyte results in several disadvantages such as high manufacturing cost, reduction of Ce^{4+} to Ce^{3+} and undesired electrode structure [6].

Two measures are usually taken in order to reach complete densification. First, the initial particle size of the powder is reduced to the nano meter range, thus increasing the driving force for sintering [7]. Second, small amounts of sintering aids such as transition metal oxides are added to increase the sintering rates. Kleinlogel and Gauckler reported the sintering of $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$ at temperatures as low as 900°C using transition metal (Ni, Cu, Co) oxide additives [5]. Work at Imperial College has confirmed these results and extended them to $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$ (CGO). Lithium oxide (LiO) was found to be a particularly effective additive in that it not only assisted densification, but also enhanced ionic conductivity in the range in which it was measured which is below 500°C.

As mention earlier, low cost production of SOFC membrane is possible through the reduction of sintering temperature. In this work, study on lowering the sintering temperature was done by manipulating mole percentage of sintering additive whereas the grain size of CGO powder was remain unchanged throughout the study. 1, 2 and 3 mole percentage of Lithium nitrate (LiNO_3) was employed as sintering additive to determine the optimum sintering temperature for the production of low cost SOFC membrane. Throughout this study, brush painting technique was applied to deposit electrolyte thin layer on anode supported hollow fibre (HF). Sintered dual layer HF membranes were compared in terms of mechanical strength (three-point bending test) and morphology (scanning electronic microscope).

2.0 MATERIALS AND EXPERIMENTAL METHODS

2.1 Materials

Commercially available 10mol% cerium-gadolinium oxide (CGO) with surface area 12 m^2/g and 192 m^2/g were purchased from Nextech Materials Ltd, and were used as supplied. Lithium nitrate (LiNO_3 , grade AR) was purchased from QREC (Asia) Sdn. Bhd and was used as supplied. Ethanol was used as solvent. The anode supported HFs used in this work were fabricated using phase inversion method as stated elsewhere [8]. The HFs precursor comprised of a mixture of NiO-CGO powders and PESf in the inner layer. As can be seen in Figure 1, the cross-section of the inner layer exhibits an asymmetric structure with short finger-like structures originating from the inner surface to approximately 35% of the inner layer thickness, whereas the other 65% consists of sponge-like structure.

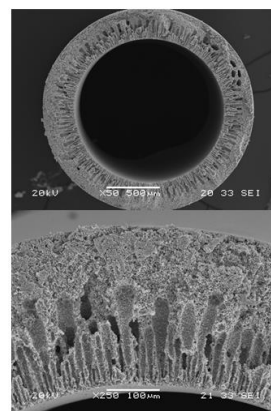


Figure 1 SEM images of NiO-CGO anode supported HF [8]

2.2 Preparation of CGO Doped Lithium Powder

In this stage, dopant was prepared by mixing 1, 2 and 3 mole percentage of LiNO_3 which is the sintering additive into CGO. Moreover, 50% nano and 50% micron size CGO powders were used throughout the study to produce dopants. The particle size of the CGO powders were remain unchanged to ensure that it does not impact on the sintering property of CGO. Appropriate amounts of LiNO_3 were weighed and dissolved in 50 mL of solvent which is deionized water using a magnetic stir bar. Appropriate amounts of nano and micron size CGO powders were then added to the nitrate solution and the solution was left for several minutes of stirring. After that, the solution was dried at 140°C for six hours to remove water and modifies the CGO powder. Schematic diagram of the procedure is shown in Figure 2.

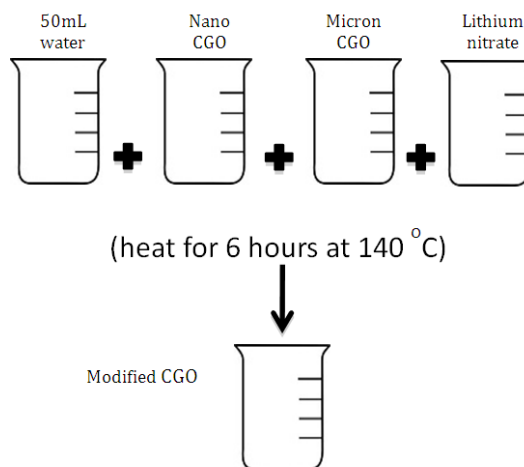


Figure 2 Preparation of CGO doped lithium powder

2.3 Deposition of Electrolyte Thin Layer on Anode Supported Hfs

In this stage, the modified CGO powder was used to make CGO slurry which later will be deposited onto anode supported HFs. Firstly, modified CGO powder was dissolved in ethanol with the mass ratio of 1:1. The mixture was stirred for several minutes to make sure the modified CGO powder disperse uniformly in ethanol. The slurry of modified CGO was then carefully deposited on the HFs using brush painting technique. Brush

painting technique is very simple and easy deposition method. The modified CGO slurry was coated three times to ensure the anode support well covered with the electrolyte layer. After each coating process, the HF's were left to dry at 80°C for five minutes. Schematic diagram of the procedure is shown in Figure 3.

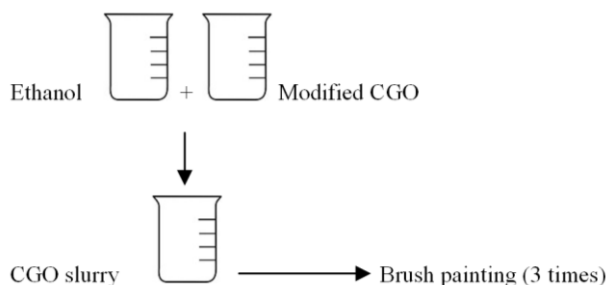


Figure 3 Deposition of electrolyte thin layer on anode supported HF

2.4 Sintering of Electrolyte Layer

In this stage, the resulting electrolyte/anode dual layer HF's were co-sintered at different temperatures to study on the sintering property of electrolyte. Total time taken for sintering was calculated based on the specific sintering profile as shown in Figure 4 and the HF's were sintered by heat treatment in a tube furnace with air flow. Sintering temperature (T_{sinter}) was varied from 1250°C to 900°C with the interval of 50°C.

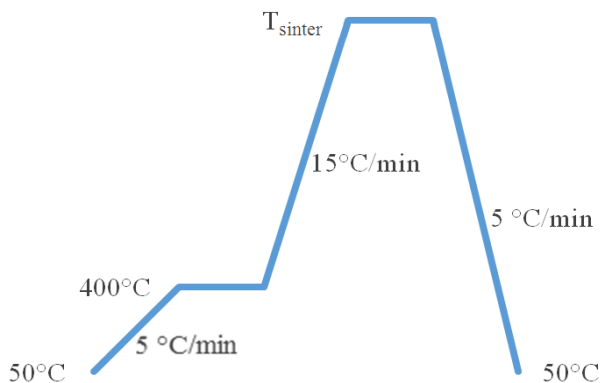


Figure 4 Applied sintering profile for the dual layer hollow fibre

2.5 Characterization of Dual Layer Hollow Fibre

In this stage, several tests were done on the sintered HF's to understand the characteristics and performances. The tests are as follow:

2.5.1 Scanning Electronic Microscope (SEM)

SEM was done on the hollow fibers to study the morphology or the structure of the HF's after sintering process. Hitachi model TM3000 was used to capture the image of HF's. The HF's snapped in order to obtain cross-sectional and surface fractures. High resolution images of the cross-section and the surface of the HF's were taken at different magnifications.

2.5.2 Mechanical Strength Analysis

The mechanical strength of HF's were examined by three-point bending test using an Instron Model 5544 tensile tester provided with load cell of 1 kN. Dual-layer HF's were fixed on the sample holder with 30 mm distance. The bending strength (σ_F) is calculated using the following equation:

$$\sigma_F = \frac{8FLD_o}{\pi(D_o^4 - D_i^4)} \quad (1)$$

where F is the measured load at which fracture occurred (N); L , D_o , D_i are the length (m), the outer diameter and the inner diameter of the HF's (m), respectively⁸.

3.0 RESULTS AND DISCUSSION

3.1 General Morphology of Dual Layer Hollow Fibre

For ceramic membranes with dual-layer structures, especially when the two layers are made of different materials, co-sintering is always challenging due to the different sintering behaviors of the membrane materials which possibly can form cracks. As for this study, the anode is made up of NiO-CGO, whereas electrolyte is made up of LiNO₃-CGO. When heat is applied, deviation in the thermal expansion coefficient of the electrolyte and anode materials can cause variations in the expansion rate. This can possibly cause the micro-cracking in the structure of electrolyte layer as shown in Figure 5. This statement is also strongly supported by the finding made in the previous studies.

Two dimensional mechanics of cracks in sintering thin films has been analyzed by Jagota and Hui [9]. They predicted condition for crack growth in sintering thin layer are related to the friction of the layer on the substrate and relative neck growth rate. However the continuous mechanic analysis has difficulty in explaining how crack initiates. In recent years, some progress has been made in the fundamental understanding of crack initiation by using discrete element modelling (DEM). For example, Henrich *et al.* [10] found that crack initiation in the constrained film is related to particle rearrangement. If rearrangement is suppressed, cracks tend to form more easily because of increased local stresses. Rasp *et al.* [11] found that particle rearrangement also affects the delamination of ceramic strips where an easier particle rearrangement inhibiting delamination at the edges of the ceramic strips (2012). The work of Martin *et al.* [12] led to the conclusion that, although geometrical constraint is necessary for a defect to grow into a crack, the presence of an initial defect is not a necessary condition to initiate cracks. Nevertheless, there is still a lack of direct experimental evidence concerning how cracking is initiated.

Figure 6 also highlights the advantage of developing dual-layer ceramic hollow fibre using brush painting technique. For most of the methods in fabricating ceramic membrane with dual-layer structure, adhesion between layers is always a big concern. As can be seen in Figure 6, great adhesion between the layers has been achieved without any delamination observed for the fabricated hollow fibres. Moreover, better adhesion also provides improved structural stability. This proves that good material compatibility between the two suspensions has been achieved through brush painting technique. This also will be very helpful during deposition of cathode layer later on. Because no quantitative adhesion measurement has ever been made on an SOFC according to open publications, no adhesion data are

available for comparison against the adhesion strengths measured in this study.

3.2 Effect of Sintering Temperature on the Microstructure of Dual-layer

For ceramic membranes, use of higher sintering temperature contributes normally in improving the mechanical strength of the membrane, while in the meantime decreases the porosity and increases the resistance to gas permeation. The dual-layer hollow fibres developed in this study is for the construction micro-tubular SOFC, which requires reasonably strong mechanical property for the deposition of remaining component such as cathode. It is also important to have a highly porous anode and dense electrolyte layer. As a result, the effects of sintering temperature on the developed dual-layer hollow fibres have been investigated.

Figure 5 illustrates evolution of the surface morphologies at different sintering temperatures between 900°C and 1250°C. It has been seen that porosities of the electrolyte layer are reduced greatly when the sintering temperature is increased.

Obvious changes in the surface morphology take place at about 1000°C, and the interconnected pores are observed from the membrane surface. When the sintering temperature increased to 1150°C, the electrolyte layer becomes almost fully dense. As the temperature goes higher, the grain size increased considerably. On further increasing the sintering temperature up to 1250°C, micro-pores clearly observed again with the possible reason of micro-cracks.

The effect of sintering temperature on the mechanical property of the developed dual-layer hollow fibre, which was investigated by a three-point bending test, is shown in Figure 7. As can be seen, a significant increase of approximately 68% in the mechanical strength was observed when the sintering temperature rises from 900 to 1100°C. In addition, sudden hike was also recorded 1150°C where the value increases by 77.4%. The optimum mechanical strength of the developed hollow fibre is 17.577 MPa which was sintered at 1150°C. At higher temperature, the ceramic particles fuse and develop into larger and closer grains with stronger bounding between them, hence giving higher mechanical strength. However, further increase in the sintering temperature would lead to micro-cracking in the structure, and thus reduce the mechanical strength, which was observed for the samples co-sintered at 1200°C and higher. This also supported by the SEM images in Figure 5, where, as the sintering temperature increases the electrolyte layer becomes denser.

3.3 Effect of Sintering Additive on the Microstructure of Dual-Layer HF

Figure 5 and 6 also illustrate the effect of sintering additives on the sintering property of the developed dual-layer hollow fibres. All the hollow fibres sintered at 900°C to 1250°C with the interval of 50°C. However, the microstructure and grain boundary phase were significantly different depending on the content of LiNO_3 . The content LiNO_3 varied from 1 to 3 mol% as sintering additive. The SEM micrograph of the hollow fibre with 1 mol% LiNO_3 reveals a microstructure consisting of fine CGO grains. Jason D. Nicholas has stated in his study that a dopant's effectiveness should simply be a matter of its ability to form a beneficial liquid phase and/or its ability to improve the CGO near grain boundary flux. It is thought that only fine grains were formed due to the insufficiency of liquid phase through which the mass transport occurred. The images also reveals the at 1 mol%

of LiNO_3 , the layer does not attain sufficient densification within 900°C to 1250°C. When the amount of LiNO_3 was increased to 2 mol%, the grains become somewhat bigger, but still dense layer was not observed. This indicates that 2 mol% LiNO_3 was still not sufficient enough for extensive growth of the CGO grains. As the amount of LiNO_3 further increased to 3 mol%, the morphology changed remarkably. Less micro pores were observed, implying 3 mol% of LiNO_3 generated a sufficient amount of liquid phase for the extensive grain growth. Based on the SEM images, sufficient densification was achieved at 1150 °C.

Figure 7 also describes the effect of LiNO_3 on the mechanical property of developed dual-layer hollow fibres. Based on the figure, as the mol% of LiNO_3 increases, the mechanical property of the hollow fibres also increases. Even though the variation is not much between 2 mol% and 3 mol%, the difference is very significant compared to 1 mol% of LiNO_3 . As the presence of LiNO_3 enables better densification, the structure becomes more stable and possesses better mechanical strength.

4.0 CONCLUSION

LiNO_3 -CGO/NiO-CGO dual-layer HFs precursors have successfully prepared by brush painting technique. The HFs precursors were then sintered at a temperature ranging from 900 to 1250°C with the interval of 50°C. The obtained dual-layer HFs possess an electrolyte layer consists of an asymmetric structure which caused by deposition technique and cracking. However, great adhesion has been achieved between anode and electrolyte layer through the brush painting technique. The experimental results obtained from the analyses conducted indicate that as the sintering temperature is increased, the densification and mechanical strength increases. The same pattern also been achieved for mol% of sintering additive, where, as the mol% of LiNO_3 increases, the densification and the mechanical strength also increases. Based on the result of this study, the recommended sintering temperature and mol% of LiNO_3 for the application of these dual-layer HFs in constructing low cost micro-tubular SOFC is 1150 °C and 3mol% of LiNO_3 respectively.

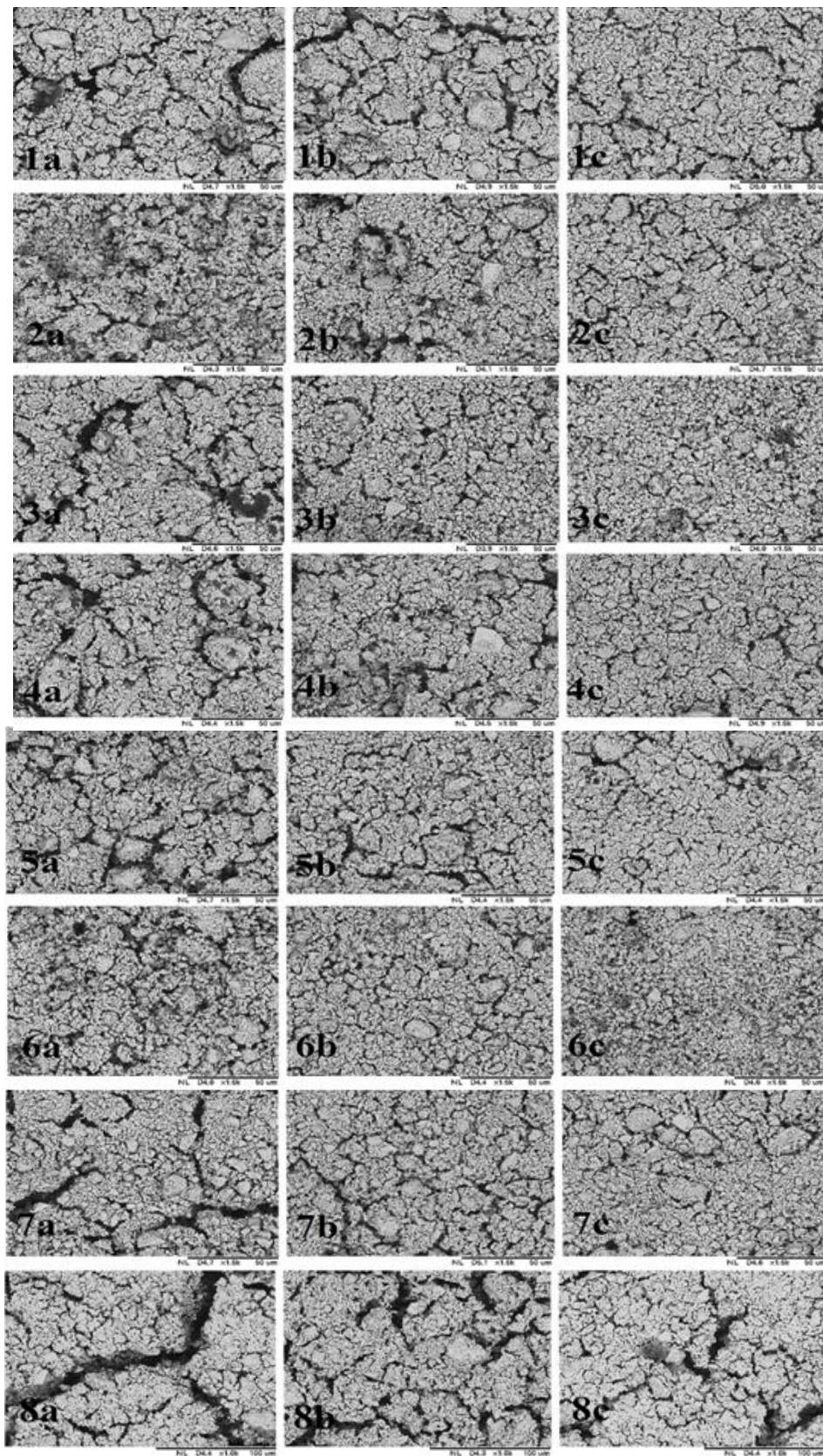


Figure 5 Surface SEM images of developed dual layer hollow fibres at different mol% of LiNO_3 : (a) 1mol%, (b) 2mol%, (c) 3mol%, at different sintering temperatures: (1) 900°C, (2) 950°C, (3) 1000°C, (4) 1050°C, (5) 1100°C, (6) 1150°C, (7) 1200°C, (8) 1250°C

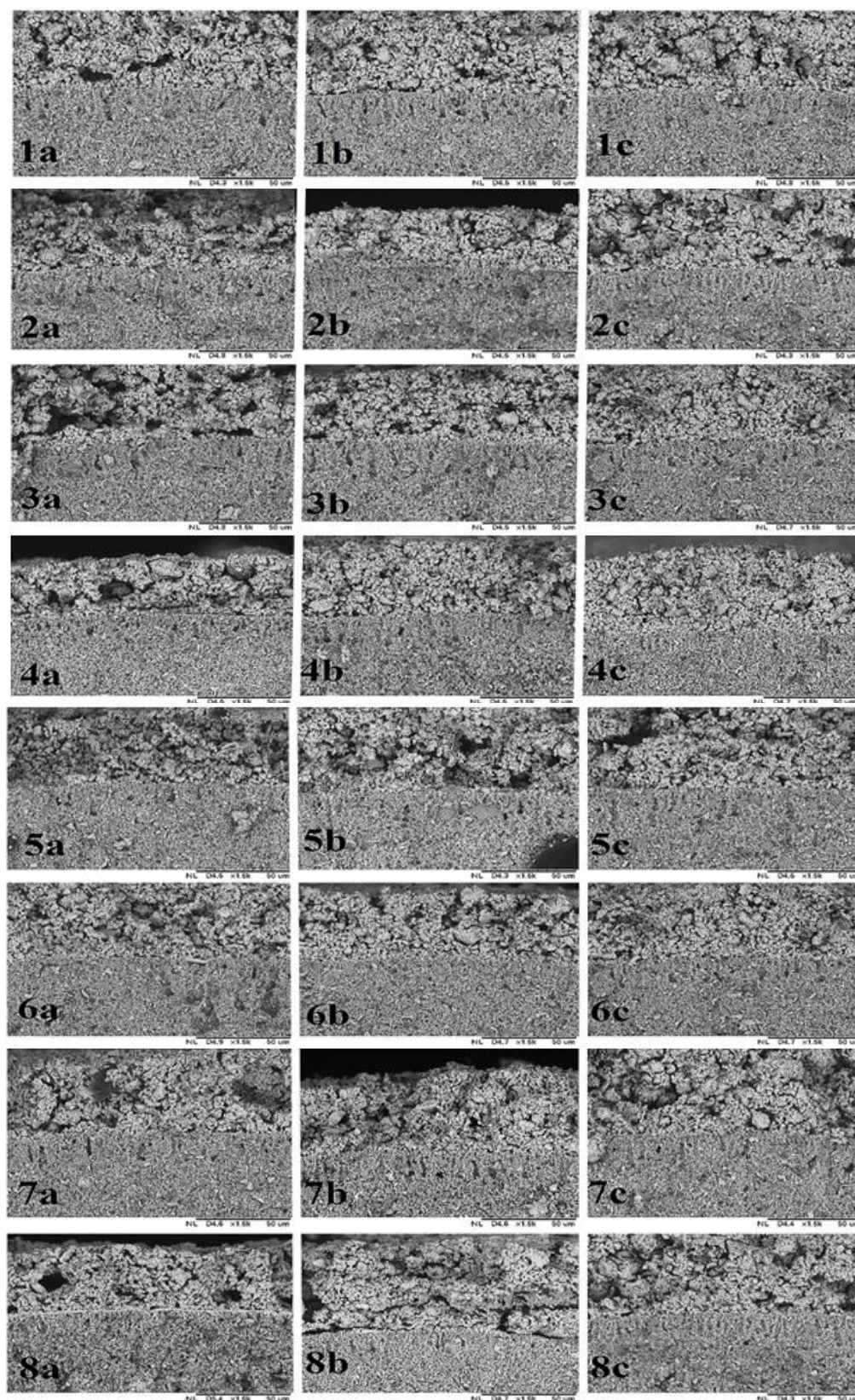


Figure 6 Cross-sectional SEM images of developed dual layer hollow fibres at different mol% of LiNO_3 : (a) 1mol%, (b) 2mol%, (c) 3mol%, at different sintering temperatures: (1) 900°C, (2) 950°C, (3) 1000°C, (4) 1050°C, (5) 1100°C, (6) 1150°C, (7) 1200°C, (8) 1250°C

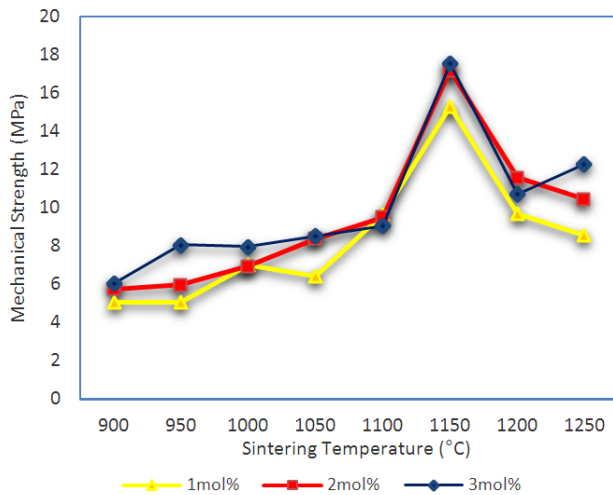


Figure 7 Bending strength of LiNO₃-CGO/NiO-CGO dual layer HFs at different sintering temperatures

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